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Three new pseudohalide bridged dinuclear Zn(II), Cd(II) complexes of pyrimidine derived Schiff base ligands: Synthesis, crystal structures and fluorescence studies

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One new dinuclear Zn(II) complex, $[(N_3)Zn(L_1)(\mu_{1,1}\text{-}N_3)]_2$ (**1**), and a dinuclear Cd(II) complex, $[(N_3)Cd(L_1)(\mu_{1,1}\text{-}N_3)]_2$ (**2**), of the potentially tridentate NNN-donor Schiff base ligand *N*-(4,6-dimethyl-pyrimidin-2-yl)-*N*′-(1-pyridin-2-yl-ethylidine)-hydrazine (L_1) and another dinuclear Cd(II) complex $[(NCS)Cd(L_2)(\mu_{1,3}\text{-}NCS)]_2$ (**3**) of a similar NNN donor Schiff base ligand, *N*-(4,6-dimethyl-pyrimidin-2-yl)-*N*′-pyridin-2-ylmethylene-hydrazine (L_2), have been synthesized and characterized by elemental analyses, IR, ^{1}H NMR, fluorescence spectroscopy and single crystal X-ray crystallography. The fluorescence spectral changes observed upon addition of the Zn(II) ion to a mixture of L_1 and azide showed high selectivity towards the Zn(II) ion over other metal ions. The ligands L_1 and L_2 are [1 + 1] condensation products of 2-hydrazino-4,6-dimethyl pyrimidine with 2-acetyl pyridine and pyridine-2-carbaldehyde, respectively. In the complexes **1** and **2** the two Zn(II) and Cd(II) centers are held together by $\mu_{1,1}$-bridged azide ions, while in **3** the two Cd(II) centers are bridged by $\mu_{1,3}$-thiocyanate ions. Complex **1** shows high chelation enhanced fluorescence compared to **2** and **3**. All the metal centers have a distorted octahedral geometry.

1. Introduction

The complexation of group 12 metal ions with polydentate Schiff base ligands is a well studied area of research in coordination chemistry [1–5]. These ligands have preparative accessibilities, structural variety and varied denticity, forming complexes of different coordination numbers and nuclearities with interesting molecular and crystalline architectures [6–16]. A substantial amount of work on pyridine and pyrazole derived Schiff base ligands have emerged in the literature, while works on pyrimidine derived Schiff base ligands are scarce. Pyrimidine derivatives play a dominant role in biological systems, the ring system being present in, for example, nucleic acids, several vitamins, co-enzymes and antibiotics [17–19]. Pyrimidine derivatives are also used in combination therapy with protease inhibitors to fight against HIV-1, the etiological agent of acquired immune deficiency syndrome [20,21]. Zn is an essential element in the biosystem. It is required in genetic materials, DNA, RNA polymerases, the regulatory Zn finger protein [structural motif for eukaryotic DNA-binding protein] in forming nucleic acids. The biological significance of Zn(II) has led to the development of numerous fluorescent chemo sensors [22]. The bioactivity of Cd is still in question, but unambiguously it is reported that the specific disease *itai itai* is caused by Cd poisoning [23,24].

As a sequel of our long standing interest in pyrimidine derived ligands [25–28] we have prepared tridentate NNN donor Schiff base ligands using 2-hydrazino-4,6-dimethyl pyrimidine and pyridine containing carbonyl compounds (2-acetyl pyridine and pyridine 2-carbaldehyde). Our interests are to observe the metal ion coordination environments and photoluminescence using 3*d*/4*d* metal ion templates, the organic ligands L_1 and L_2, and suitable bridging units. We choose zinc and cadmium because the d^{10} configuration in zinc permits a wide range of symmetries and various coordination numbers, i.e., 4, 5 or 6, relatively easily [29–31], while cadmium shows 4, 6, 7 coordination. Moreover, luminescent compounds are attracting much current research interest because of their many applications, including emitting materials for organic light emitting diodes, light harvesting materials for photo catalysis and fluorescent sensors for organic or inorganic analyses [32]. Introduction of electron-donating groups into the Zn(II) complexes enhances the quantum yield of the photoluminescence [33]. Hence it is important to understand the coordination chemistry and luminescence between group 12

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metal ions for developing new materials which can function as fluorescent sensors [32]. In the present study (Scheme 1), using zinc perchlorate and cadmium perchlorate as the metal precursors, one new dinuclear zinc(II) complex $[(N_3)Zn(L_1)(\mu_{1,1}\text{-}N_3)]_2$ (**1**) and two new dinuclear cadmium(II) complexes, $[(N_3)Cd(L_1)(\mu_{1,1}\text{-}N_3)]_2$ (**2**) and $[(NCS)Cd(L_2)(\mu_{1,3}\text{-}NCS)]_2$ (**3**), have been synthesized with L_1 and L_2. We have reported the synthetic details, spectral characterizations, X-ray crystal structures and fluorescence studies of **1**, **2** and **3**, where pseudohalides act as terminal ligands as well as bridging ligands ($\mu_{1,1}$; $\mu_{1,3}$) in presence of the ligands L_1 and L_2.

2. Experimental

2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. 2-Acetyl pyridine, pyridine-2-carbaldehyde and methyl cyclohexane were purchased from the Aldrich Chemical Company, USA and used without further purification.

Caution! Although we have not encountered any problems, it should be kept in mind that sodium azide and perchlorate compounds of metal ions are potentially explosive, especially in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical measurements

The infrared spectra of the complexes were recorded on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr discs (4000–300 cm^{-1}). Elemental analyses (C, H and N) were carried out using a Perkin-Elmer 2400 II elemental analyzer. ^1H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as an internal standard in d_6-DMSO for complexes **1**, **2** and **3**. Steady state absorption and fluorescence spectra for all three complexes and the Schiff base ligands were measured with a Hitachi UV–Vis U-3501 spectrophotometer and a Perkin-Elmer LS50B fluorimeter, respectively, at room temperature (298 K). All the spectral measurements were done at $\sim 10^{-5}$ to 10^{-6} (M) concentration of solute in order to avoid aggregation and self-quenching.

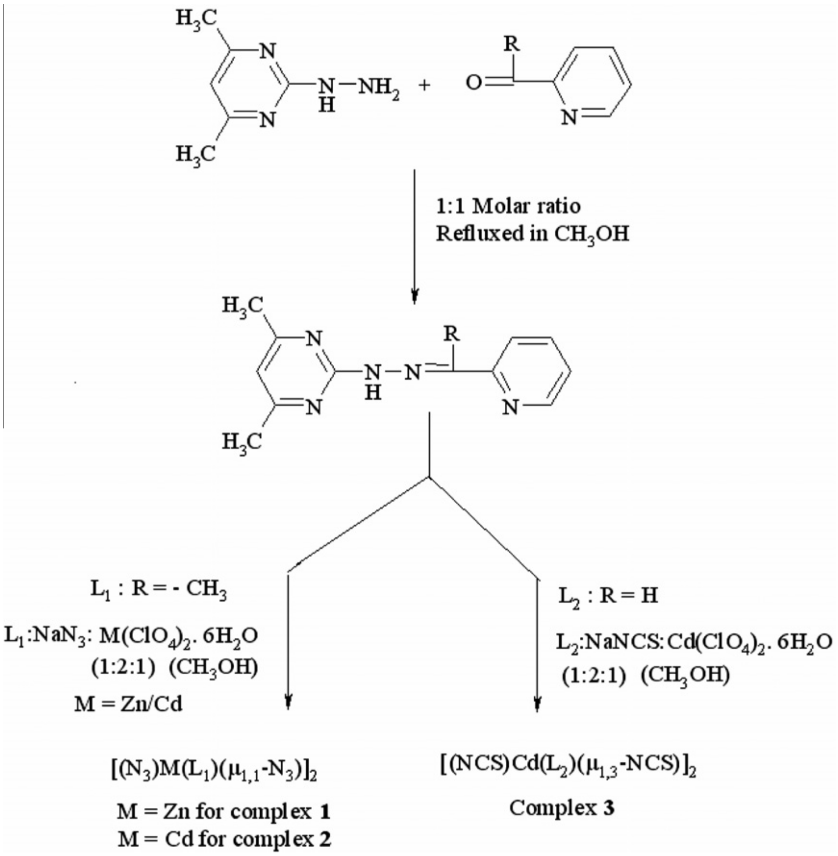
Fluorescence quantum yields of the zinc and cadmium pseudohalide complexes of the ligands were calculated using β-naphthol as the reference with a known Φ_f (0.23) in MCH solvent, using the following equation [34,35]

$$\Phi_f = \Phi_f^0 \frac{n_f^2 A \int I_f^0(\lambda_f)d\lambda_f}{n_{0f}^2 A^0 \int I_f(\lambda_f)d\lambda_f}$$

Here n_0 and n are the refractive indices of the solvents, A^0 and A are the absorbance's, Φ_f^0 and Φ_f are the quantum yields, and the integrals denote the area of the fluorescence band for the standard and the sample, respectively.

2.3. Syntheses of the ligands (L_1 and L_2)

The ligand L_1 was synthesized by refluxing a methanol solution (30 ml) of 2-hydrazino-4,6-dimethyl pyrimidine [36,37] (1.38 g, 10 mmol) with 2-acetyl pyridine (1.21 g, 10 mmol) taken in the same solvent. The refluxing was continued for 1 h at water bath temperature. The resulting light yellow solution was filtered and kept at room temperature for slow evaporation. A light yellow microcrystalline compound separated after a week. It was filtered



Scheme 1.